TKK Radio Science and Engineering Publications
Espoo, March 2008 REPORT R1

MODELING OF ELECTRICAL PROPERTIES OF COMPOSITES

Thesis for the degree of Doctor of Science in Technology

Liisi Jylhä

Dissertation for the degree of Doctor of Science in Technology to be presented with due permission of the Faculty of Electronics, Communications and Automation, for public examination and debate in Auditorium S 4 at Helsinki University of Technology (Espoo, Finland) on the 14th of March, 2008, at 12 noon.

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ISBN 978-951-22-9237-0 (printed)
ISBN 978-951-22-9238-7 (electronic)
http://lib.tkk.fi/Diss/2008/isbn9789512292387
ISSN 1797-4364

Picaset Oy
Helsinki 2008

ABSTRACT OF DOCTORAL DISSERTATION	HELSINKI UNIVERSITY OF TECHNOLOGY P.O. BOX 1000, FI-02015 TKK http://www.tkk.fi

Author Liisi Jylhä

Name of the dissertation
Modeling of electrical properties of composites

Manuscript submitted 22nd October .2007	Manuscript revised 21st February 2008
Date of the defence 14th March 2008	
☐ Monograph	☒ Article dissertation (summary + original articles)

Faculty	Faculty of Electronics, Communications and Automation
Department	Department of Radio Science and Engineering
Field of research	Electromagnetics
Opponent(s)	Doctor Luk Arnaut
Supervisor	Academy professor Ari Sihvola
Instructor	Academy professor Ari Sihvola

Abstract

Composites offer a way to design electromagnetic properties simultaneously with other material properties such as mechanical or thermal properties. This thesis describes studies pertaining to the modeling of effective electrical material properties of artificial composites of two separate material phases. This has practical importance because modeling reduces experimental effort when developing novel composites or improving the existing ones. The focus is on materials which have a disordered microstructure, and the scale of inhomogeneities is much smaller than the wavelength.

In this thesis, a historical overview about modeling of electrical properties of composites is given. Then a novel method to reduce the computational cost of numerical modeling is introduced. Results are compared to experiments with polymer/ceramic composites. Some problems related to the modeling of the effective permittivity are also pointed out. Novel analytical methods for the modeling of electrical properties of composites are introduced. An equation, which combines desirable properties of two popular mixing equations, is derived. A new method to calculate the effective permittivity and the tunablity of a composite consisting of linear and non-linear dielectrics is given.

Keywords	composite, permittivity, permeability, conductivity, microstructure, random
ISBN (printed) 978-951-22-9237-0	ISSN (printed) 1797-4364
ISBN (pdf) 978-951-22-9238-7	ISSN (pdf)
Language English	Number of pages 44 p. + app. 50 p.
Publisher	Helsinki University of Technology, Department of Radio Science and Engineering
Print distribution	Helsinki University of Technology, Department of Radio Science and Engineering

☒ The dissertation can be read at http://lib.tkk.fi/Diss/

VÄITÖSKIRJAN TIIVISTELMÄ	TEKNILLINEN KORKEAKOULU PL 1000, 02015 TKK http://www.tkk.fi
Tekijä Liisi Jylhä	
Väitöskirjan nimi Modeling of electrical properties of composites	
Käsikirjoituksen päivämäärä 22.10.2007	Korjatun käsikirjoituksen päivämäärä 21.2.2008
Väitöstilaisuuden ajankohta 14.3.2008	
☐ Monografia	☒ Yhdistelmäväitöskirja (yhteenveto + erillisartikkelit)

Tiedekunta	Elektroniikan, tietoliikenteen ja automaation tiedekunta
Laitos	Radiotieteen ja -tekniikan laitos
Tutkimusala	Sähkömagnetiikka
Vastaväittäjä(t)	Tohtori Luk Arnaut
Työn valvoja	Akatemiaprofessori Ari Sihvola
Työn ohjaaja	Akatemiaprofessori Ari Sihvola

Tiivistelmä

Komposiitit mahdollistavat sähkömagneettisten ominaisuuksien ja muiden ominaisuuksien, kuten mekaanisten ja termisten, yhtäaikaisen suunnittelun. Tämä väitöskirja käsittelee keinotekoisten, kahdesta erillisestä materiaalista koostuvien komposiittien mallintamista. Tällä on käytännön merkitystä, koska mallintaminen pienentää kokeellista työmäärää kun uusia materiaaleja kehitetään tai olemassaolevia parannetaan. Painopiste on materiaaleissa, joilla on paljon aallonpituutta pienempi, epäsäännöllinen hienorakenne.

Tässä väitöskirjassa esitellään aluksi historiallisia mallinnustapoja komposiittien sähköisille ominaisuuksille. Työssä on kehitetty uusi menetelmä, joka vähentää numeerisen laskennan kustannusta. Tuloksia verrataan kokeisiin polymeeri/keraami-komposiiteilla. Myös joitakin mallinnukseen liittyviä ongelmia tarkastellaan. Työssä tutkitaan uusia analyyttisia menetelmiä komposiittien sähköisten ominaisuuksien mallintamiseksi ja esitellään uusi yhtälö joka yhdistää kahden suositun sekoitusteorian tulokset. Lisäksi työssä on johdettu uusi menetelmä laskea lineaarisesta ja epälineaarisesta eristeestä koostuvan komposiitin efektiivinen permittiivisyys ja säädettävyys.

Asiasanat komposiitti, permittiivisyys, permeabilisuus, johtavuus, mikrorakenne, satunnainen	
ISBN (painettu) 978-951-22-9237-0	ISSN (painettu) 1797-4364
ISBN (pdf) 978-951-22-9238-7	ISSN (pdf)
Kieli englanti	Sivumäärä 44 s. + liit. 50 s.
Julkaisija Teknillinen korkeakoulu, radiotieteen ja -tekniikan laitos	
Painetun väitöskirjan jakelu Teknillinen korkeakoulu, radiotieteen ja -tekniikan laitos	
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Preface

This thesis is the result of studies that began in 1999, when Prof. Ari Sihvola agreed to supervise me in the field of electromangetics and materials. I wish to express my gratitude for receiving his guidance throughout the years. I wish to thank Prof. Heli Jantunen for her support and instruction in the field of material science and Johanna Honkamo for co-operation and her guidance on chemistry. Also, I am very grateful to Prof. Jin Au Kong and the Graduate School of Electronics, Telecommunications and Automation (GETA) for the opportunities to visit Zhejiang University of Technology in China and Massachusetts Institute of Technology in USA. I wish to thank for the privilege of receiving valuable instructions and teahcing from Prof. Jukka Sarvas, Prof. Ismo Lindel, Prof. Keijo Nikoskinen, Prof. Sergei Tretyakov and Dr. Thomaz Gregorzyk. I wish to thank Katrina Nykänen and the staff of the former Electromagnetics Laboratory and the Department of Radio Science and Engineering. The Vilho, Yrjö and Kalle Väisälä Foundation, Jenny and Antti Wihuri Foundation of Science and Letters and GETA are cordially thanked for the financial support for this work.

A lot of thanks to Juhana Schulman and my family Marja-Liisa, Tapani and Juho Jylhä, and all the friends for meeting the adventures of life with me.

Helsinki, February 2008 Liisi Jylhä

Contents

List of publications

[P1] L. Jylhä and A. Sihvola, "Numerical modeling of disordered mixture using pseudorandom simulations", *IEEE Transactions on Geoscience and Remote Sensing*, Vol. 43, No. 1, pp. 59–64, 2005.

[P2] L. Jylhä, Johanna Honkamo, Heli Jantunen and A. Sihvola, "Microstructure-based numerical modeling method for effective permittivity of ceramic/polymer composites", *Journal of Applied Physics*, Vol. 97, 104104, 2005.

[P3] L. Jylhä and A. Sihvola, "Approximations and full numerical simulations for the conductivity of three dimensional checkerboard geometries", *IEEE Transactions on Dielectrics and Electrical Insulation*, Vol. 13, No. 4, pp. 760–764, 2006.

[P4] L. Jylhä and A. Sihvola, "Equation for the effective permittivity of particle-filled composites for material design applications", *Journal of Physics D: Applied Physics*, Vol. 40, pp. 4966–4973, 2007

[P5] L. Jylhä and A. Sihvola, "Tunability of granular ferroelectric dielectric composites", *Progress in Electromagnetic Reseach*, Vol. 78, pp. 189–207, 2008.

All papers [P1-P5] are mainly written by the author. In [P1] Professor Ari Sihvola presented the idea of calculating the effective permittivity of random mixtures and the author performed numerical simulations. The author found out that the averaging method reduced the computational effort, which is the main result of the paper. In [P2] professor Heli Jantunen suggested to test the method presented in [P1] with ceramic polymer composites. All numerical and analytical modeling was performed by the author. Samples were manufactured and tested by Johanna Honkamo. Numerical simulations in [P3] were made by the author to demonstrate problems related to so-called connectivity approach. The analytical models in [P4] and [P5] were developed by the author.

1 Introduction

Electromagnetic properties of a material arise from its microscopic structure [1,2]. In a homogenous material, the material response to the electromagnetic field depends on the atomic or molecular structure. A heterogeneous material consists of inhomogeneities in a larger scale than the atomic scale. In this thesis, this kind of structure is referred to as composite material. Composites are studied that consist of two separate material phases with well distinguished material boundaries. When the scale of the discontinuities is much smaller than the wavelength, effective electromagnetic properties can be defined.

Composites produce a large variety of new materials. They offer a way to combine the required electromagnetic properties with other material properties. There are several handbooks about the macroscopic electrical properties of composite materials [3–9]. This thesis describes study pertaining to the modeling of effective electrical material properties of artificial composites consisting of two separate material phases. The focus is on materials, which have a disordered microstructure. These materials can be manufactured for example by mixing two ceramic powders and melting the powder to form a solid ceramic composite. Ceramic powder can also be mixed with polymer in an extruder. Both of these processes can lead to a disordered microstructure. An example of such a material is shown in Fig. (1). In this case, the titanium dioxide powder shown in Fig.(2) is mixed with epoxy.

The development of novel technologies requires a wide range of materials with varying electromagnetic properties. Also other properties such as thermal or mechanical properties are at least as important. In some applications, materials with the best electromagnetic properties cannot be applied. They are potentially too expensive or impossible to process because of their mechanical properties. For example, the recent development of the low temperature cofired ceramic (LTCC) technique requires laminates or tapes between ceramic sheets, which are melted and pressed together [10–12]. In this example, the electromagnetic properties are very important for the function of the final product, but only those materials which are suitable for the manufacturing process can be considered. Another limitation is the cost of the material. There might be available materials, which electromagnetic properties are outstanding, but they cannot be applied because of their high cost. Also in this case, it might be relevant to seek alternative options. The topic of this thesis has practical importance, because the modeling of composite materials reduces the experimental effort when developing novel composites or when improving the existing ones.

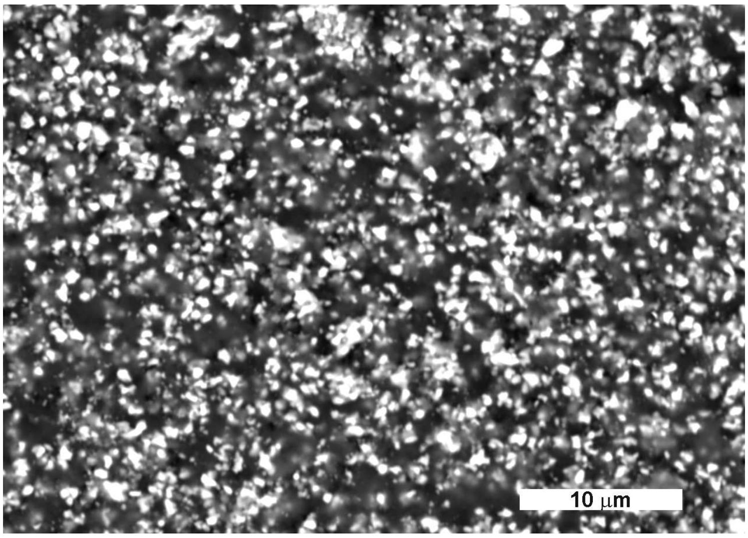


Figure 1: Scanning electron microscope picture of ceramic powder mixed with epoxy. Ceramic inclusions are in the scale of micrometer.

There is a need to find the most suitable modeling methods for composite designing applications by taking into account the special features of such materials. Methods should be suitable for modeling the effective permittivity with all volume fractions of inclusions that can be manufactured in practice. Furthermore, they should be applicable for material combinations that have a large electrical contrast. This thesis describes how existing modeling techniques are improved and new analytical methods are developed.

Composites of linear dielectric and ferroelectric are also discussed in this thesis. Ferroelectric materials are materials in which permittivity can be changed by a biasing electric field. The permittivity of the ferroelectric depends nonlinearly on the biasing field. They have many important applications. For example, ferroelectric capacitors are used to make ferroelectric RAM for computers and in radio frequency identification (RFID) cards. The permittivity of the ferroelectric ceramics is extremely high, several thousands. Sometimes this is a disadvantage. It can cause cross talking in integrated circuits and reduce the signal velocity. There are organic ferroelectric materials [13, 14] with low permittivity in the order of ten. Problems with these materials are high losses and a low switching time, which highly restrict their use in the radio frequency range [15]. A possible solution for the requirement of tunable low-permittivity materials is a ferroelectric-polymer or ferroelectric-ceramic composite [16–20]. They are also suitable for altering the mechanical properties of ferroelectric

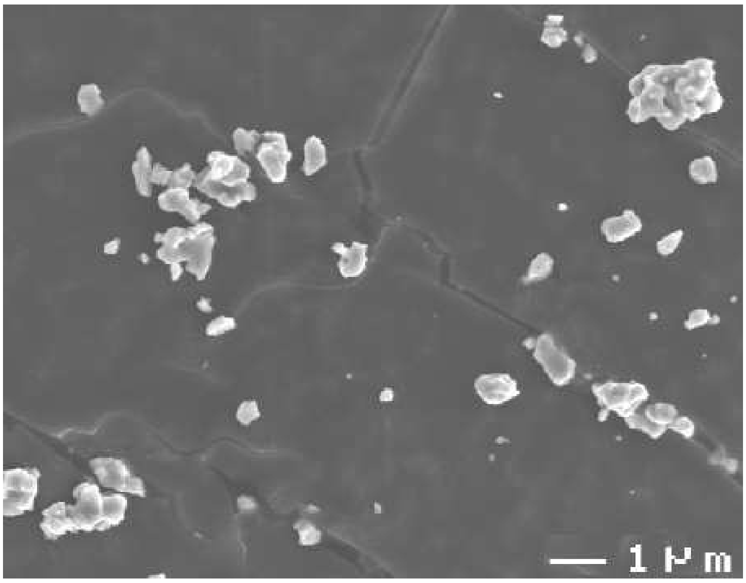


Figure 2: Scanning electron microscope picture of ceramic powder before mixing.

ceramics to allow the use of the ferroelectric materials in new applications. In this thesis, a novel equation for calculating the effective permittivity and tunability of composites is developed.

Throughout the thesis, the modeling of the effective permittivity is considered. Results are also applicable for modeling the effective permeability, the effective electric conductivity or the effective heat conductivity of the material.

2 Review to electromagnetic modeling of composites

In this section, analytical and numerical methods to model the effective permittivity of composites are introduced. The possible restrictions and problems related to the methods are pointed out.

2.1 Homogenization

The electrical response of a material to the electric field can be described with the complex permittivity $\varepsilon = \varepsilon' - j\varepsilon''$. The real part of the complex permittivity is a measure of the ability of a dielectric to store electrical energy and the imaginary part is a measure of the ability to absorb energy. The electrical energy can be lost by the conducting currents or by friction involved in the polarization of molecules or atoms.

This thesis focuses on low loss dielectric materials. For low loss materials, the real part of the permittivity is much larger than the imaginary part $\varepsilon' >> \varepsilon''$. In other words, they are good insulators. They have significant practical importance, because low losses reduce the amount of power transferred into heat. Low losses improve, for example, the quality factor of a resonator.

The permittivity of a homogenous material is defined by its atomic structure. The effective permittivity of a composite material is also defined by the structure. If the composite consist of two or more homogenous materials and there are boundaries between these material phases, then there are polarization mechanisms in the scale of inhomogeneities in addition to polarization mechanisms related to individual atoms and molecules. On the left side of Fig. 3, an illustration of a composite material is presented. In this case, black inclusions with permittivity ε_{i} are randomly dispersed into the white background with permittivity ε_{e} . To highlight the possibility that the composite can have any mixing ratio between white and black inclusions, the boundaries between the white inclusions are shown.

If the scale of inhomogeneities in the mixture is much smaller than the

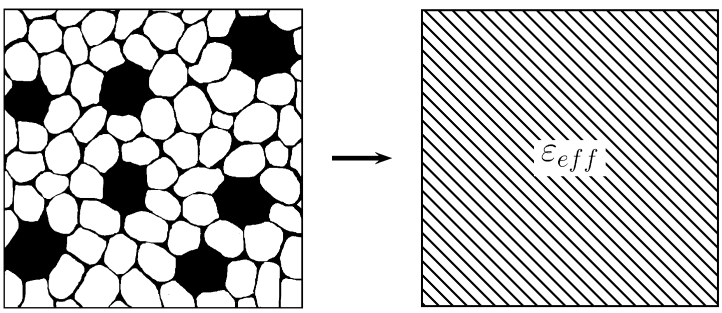


Figure 3: Illustration of the homogenization of a two phase composite.

wavelength inside the mixture, one can define the effective permittivity for the material ε_{eff}. The effective permittivity can be defined in a case, where the electromagnetic field does not 'see' the inhomogeneities in the material. When a piece of such a composite is placed in the electromagnetic field, the electromagnetic field scatters as it would scatter from an object with the permittivity equal to the effective permittivity ε_{eff}. At the GHz or MHz frequency range, the wavelength is measured in a scale of centimeters or meters. At these frequencies, the effective permittivity can be defined for all non-resonant materials with microscopic inhomogeneities.

When the effective permittivity can be estimated using either analytical or numerical methods, the designing of new materials is easier than it would be solely experimentally. In practice, modeling the effective permittivity is very complex. The effective permittivity is a function of the volume fraction of the constitute materials and the permittivities of both materials. It is also a function of the geometry of the structure and sometimes also a function of the scale of the inhomogeneities.

2.2 Analytical methods

In this section, the most widely used analytical models for the effective permittivity of a mixture with disordered microstructure are introduced.

There are several good methods of fitting a semi-empirical model involving adjustable parameters to measurement results, such as [21–26]. However, if one is interested in general principles of how to choose the best material combination for a given application, the choice of the adjustable parameters is problematic. Parameters in the models do not have a simple link to some physical parameters. As a result, they only offer a little help when measurement results for the studied material combination are not available.

In this thesis, the focus is on models that do not include adjustable parameters. Parameters that are included are the permittivity of mixed materials, the volume fraction of inclusions and the shape of inclusions. When the permittivity of the mixed materials depends also on the temperature and frequency, the dependence of the effective permittivity on these parameters can also be modeled.

2.2.1 Spherical inclusions

Homogenization of a mixture of spheres is illustrated in Fig. 4. If the distance between each sphere compared with radii, the effective permittivity can be calculated accurately. In that case the effective permittivity of the composite does not differ much from the permittivity of the background. When spheres are closely packed, calculating the effective permittivity becomes more complicated.

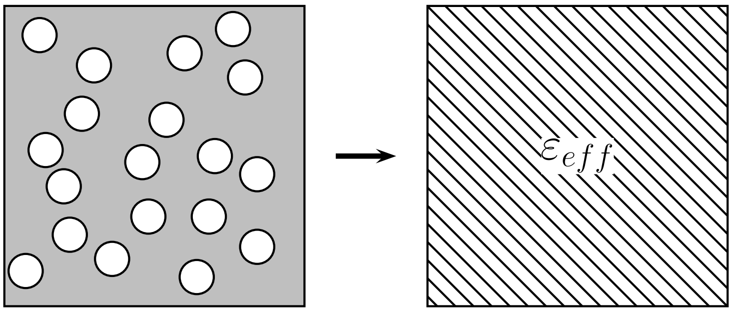


Figure 4: A two phase mixture of homogenous spheres in the homogenous background.

A list of classical mixing equations discussed in this section is presented in Table 2.2.1, where ε_i is the permittivity of spheres, ε_e is the permittivity of the environment and f is the volume fraction of spheres. Maxwell Garnett (MG) [27] and Bruggeman symmetric (BS) [28] are studied more closely. They are, perhaps, the most popular mixing equations.

Maxwell Garnett (MG)

The Maxwell Garnett mixing equation can be derived by replacing each sphere with an equivalent dipole moment [27, 29–31]. By adding the contribution of all dipoles together, the effective permittivity can be calculated.

When a small sphere is placed in an electric field, it can be replaced with an electric dipole with a dipole moment

$$p = \alpha E_L \tag{1}$$

where E_L is the local electric field on the sphere and α is the polarizability of

$\varepsilon_{\text{eff}} = \varepsilon_{\text{e}} + 3f\varepsilon_{\text{e}}\dfrac{\varepsilon_{\text{i}} - \varepsilon_{\text{e}}}{\varepsilon_{\text{i}} + 2\varepsilon_{\text{e}} - f(\varepsilon_{\text{i}} - \varepsilon_{\text{e}})}$	(MG)
$\dfrac{\varepsilon_{\text{i}} - \varepsilon_{\text{eff}}}{\varepsilon_{\text{i}} + 2\varepsilon_{\text{eff}}}f + \dfrac{\varepsilon_{\text{e}} - \varepsilon_{\text{eff}}}{\varepsilon_{\text{e}} + 2\varepsilon_{\text{eff}}}(1-f) = 0$	(BS)
$\varepsilon_{\text{eff}} = \varepsilon_{\text{e}} + f(\varepsilon_{\text{i}} - \varepsilon_{\text{e}})\dfrac{3\varepsilon_{\text{eff}}}{3\varepsilon_{\text{eff}} + (1-f)(\varepsilon_{\text{i}} - \varepsilon_{\text{e}})}$	(CP)
$\dfrac{\varepsilon_{\text{i}} - \varepsilon_{\text{eff}}}{\varepsilon_{\text{i}} - \varepsilon_{\text{e}}} = (1-f)\left(\dfrac{\varepsilon_{\text{eff}}}{\varepsilon_{\text{e}}}\right)^{1/3}$	(BN)
$\dfrac{\varepsilon_{\text{eff}} - \varepsilon_{\text{e}}}{\varepsilon_{\text{i}} - \varepsilon_{\text{e}}} = f\left(\dfrac{\varepsilon_{\text{eff}}}{\varepsilon_{\text{i}}}\right)^{1/3}$	(SSC)
$\varepsilon_{\text{eff}}^{1/3} = (1-f)\varepsilon_{\text{e}}^{1/3} + f\varepsilon_{\text{i}}^{1/3}$	(LO)
$\log\varepsilon_{\text{eff}} = f\log\varepsilon_{\text{i}} + (1-f)\log\varepsilon_{\text{e}}$	(LI)

Table 1: Classical mixing theories for random mixtures of spherical inclusions. See text for abbreviations.

the sphere

$$\alpha = V(\varepsilon_{\text{i}} - \varepsilon_{\text{e}})\frac{3\varepsilon_{\text{e}}}{\varepsilon_{\text{i}} + 2\varepsilon_{\text{e}}} \tag{2}$$

where ε_{e} is the external permittivity around the sphere, ε_{i} is the internal permittivity of the sphere, and V is the volume of the sphere. These equations hold when the electric field acting on the sphere is homogenous and the wavelength is much longer than the diameter of the sphere.

The effective permittivity ε_{eff} of a mixture of spheres can be defined as

$$D_{\text{ave}} = \varepsilon_{\text{eff}}E_{\text{ave}} = \varepsilon_{\text{e}}E_{\text{ave}} + P_{\text{ave}} \tag{3}$$

where D_{ave} is the global average electric flux density, E_{ave} is the global average electric field and P_{ave} is the average electric polarization density: $P_{\text{ave}} = n\mathbf{p}$, where n is the number density of spheres.

The local electric field acting on each sphere can be written as

$$E_L = E_{\text{ave}} + \frac{1}{3\varepsilon_{\text{e}}} P_{\text{ave}} \tag{4}$$

where 1/3 arises from the depolarization factor of a sphere. This equation holds if the spheres are well separated, because then the effect of other dipoles can be taken into account with a simple summation of their far fields. The effective permittivity solved from Eqs. (1)–(4) with $f = nV$ is called the Maxwell Garnett mixing equation (also known as the Clausius-Mossotti equation). It is presented in Table 2.2.1 as (MG). The small volume fraction limit of MG is

$$\varepsilon_{\text{eff}} \approx \varepsilon_{\text{e}} + n\alpha \tag{5}$$

This is tantamount to replacing the local field in (1) with the global average field E_{ave}. In other words, the dipole moment of a sphere is not affected by other spheres. This is the correct low volume filling ratio limit, because there the dipole moment of each sphere approaches the dipole moment of isolated spheres when the volume filling ratio of the spheres approaches zero. When studying the Taylor series of the MG equation, it has been shown that there are more correct terms in the equation than the small volume fraction limit of (5) for regular lattices of spheres [32, 33]. Analytical solutions at quasi static limit for lattices of spheres have also been presented in citemeredith, doyle, mcphedran. According to numerical studies, the MG mixing equation seems to be in agreement with the simulations also conducted for random arrangement of spheres [34].

With large volume fractions of spheres MG seems to underestimate the effective permittivity of random mixtures (see for example [35, 36]), because it has a percolation threshold of $f = 1$. That is to say that in the case of high electrical contrast, the effective permittivity is closer to the permittivity of the background until the mixture is almost completely filled with spheres. At that point, the effective permittivity rapidly approaches the permittivity of the spheres. If inclusions were ideally conductive, then below the percolation threshold, the composite is an insulator and above the threshold it is a conductor. Percolation threshold is a critical volume fraction of metal in the composite at which the metal phase becomes connected and the effective conductivity increases rapidly.

Bruggeman symmetric (BS)

Another popular mixing equation is the symmetric Bruggeman equation (BS) [28,37–39]. This is also often called an effective medium approximation (EMA)

[40], although the name is sometimes used with any mixing equation. The (BS) is derived by assuming the symmetry between the inclusion and the environment phases. The first term in the summation represents the polarizability of a sphere with permittivity ε_{i} weighted with the volume fraction of the material with ε_{i}. The second term represents the polarizability of a sphere with permittivity ε_{e} weighted with the volume fraction of the material with ε_{e}.

This equation is popular, because it often gives a reasonable estimate for composites with all volume fractions of spherical-like inclusions, which is important when one material phase does not dominate the composite [34, 41]. The Bruggeman formula predicts close to the same effective permittivity with small volume fractions of inclusions as MG does. However, when the contrast between permittivities ε_{e} and ε_{i} is large, MG and BS give the same approximation with only very small volume filling ratios of inclusions.

One problem with the BS mixing equation is that it tends to overestimate the effective permittivity of a random mixture of spheres with small volume fractions of spheres. In that case the effective permittivity can be predicted better with the MG equation. Another problem with BS equation is that the percolation threshold of spheres with equal radius is $f = 0.33$. Sometimes this is a problem with real life composites where the percolation can have a significantly different threshold. However, this problem could be avoided by using the Bruggeman symmetric formula for ellipsoidal inclusions.

Other mixing equations and examples

The so-called coherent potential formula has also the same derivative as MG and BS with small volume filling ratios of spheres. It is not as popular as BS or MG, because it predicts larger permittivities than both of them [42, 43]. It is marked with (CP) to Table 2.2.1.

Another class of mixing formulas is derived with differential analysis. They share the common property that the permittivities are raised to powers of one third. Four differential-based formulas are given in the Table 2.2.1: Bruggeman non-symmetric (BN) [28], Sen-Scala-Cohen (SSC) [44], Looyenga (LO) [45] and Lichtenecker (LI) [9,46]. In [47] it is shown that if the basic MG or symmetric Bruggeman rules are used in an iterative scheme, the result leads to the non-symmetric Bruggeman case.

An example of the predictions from different mixing equations is presented in

Fig. 5 and Fig. 6 for a mixture of spheres with permittivity 50 in a background with permittivity 1. The effective permittivity as a function of volume filling ratios of spheres is presented for the mixing equations in the Table 2.2.1.

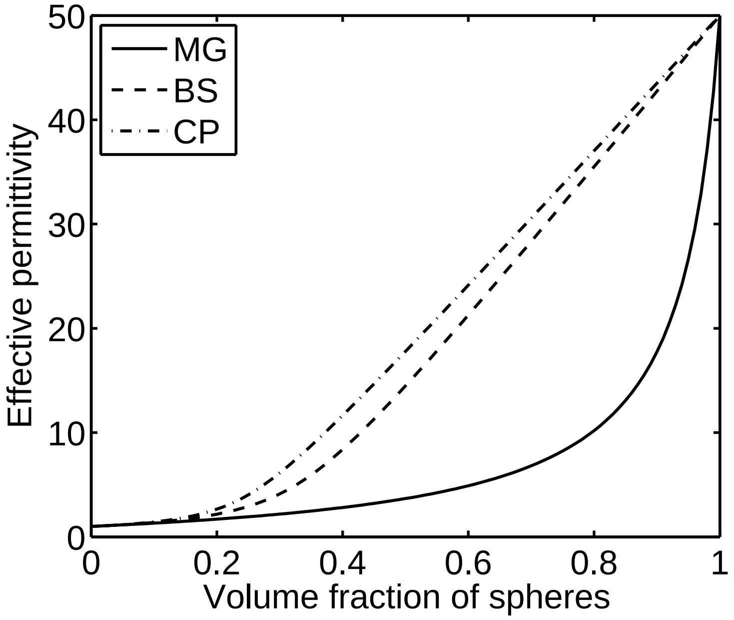


Figure 5: Effective permittivity as a function of the volume filling ratio of spheres according to MG, BS and CP equations from Table 2.2.1 The permittivity of the spheres is 50 and that of the background is 1.

2.2.2 Ellipsoidal inclusions

The effective permittivity of a mixture of spheres is derived by replacing each sphere with a dipole, which dipole moment depends on the polarizability of a sphere. More general mixing formulas can be written, when the mixture is assumed to consist of randomly oriented ellipsoids [3, 48, 49].

Polarizability can be solved with depolarization factors. They are denoted by $N_{x,y,z}$. For spheres these are $N_x = N_y = N_z = 1/3$. The depolarization factors for general ellipsoids contain elliptic integrals [50] but for spheroids, closed-form expression can be written: for prolate spheroids ($a_z > a_x = a_y$),

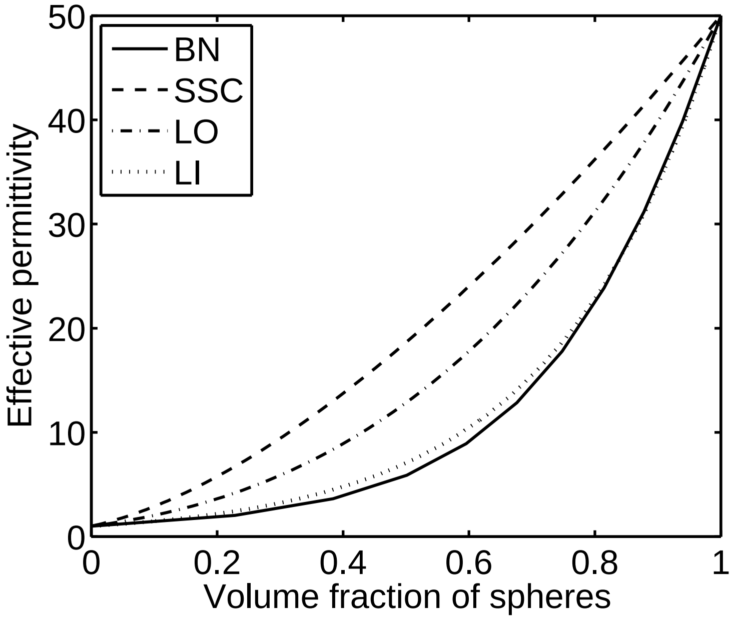


Figure 6: Effective permittivity as a function of the volume filling ratio of spheres according to BN, SSC, LO and LI equations from Table 2.2.1.

the depolarization factors are

$$N_z = \frac{1-e^2}{2e^3}\left(\ln\frac{1+e}{1-e} - 2e\right), \qquad N_x = N_y = \frac{1}{2}(1-N_z) \tag{6}$$

where the eccentricity is $e = \sqrt{1 - a_x^2/a_z^2}$. For oblate spheroids ($a_z < a_x = a_y$),

$$N_z = \frac{1+e^2}{e^3}\left(e - \tan^{-1} e\right), \qquad N_x = N_y = \frac{1}{2}(1-N_z) \tag{7}$$

where $e = \sqrt{a_x^2/a_z^2 - 1}$, with a_x, a_y and a_z being the three semiaxes of the ellipsoid. Depolarization factors for any ellipsoid satisfy $N_x + N_y + N_z = 1$.

The Maxwell Garnett equation for the effective permittivity reads [3]

$$\varepsilon_{\text{eff}} = \varepsilon_{\text{e}} + \varepsilon_{\text{e}} \frac{\frac{f}{3}\sum\limits_{j=x,y,z} \frac{\varepsilon_{\text{i}} - \varepsilon_{\text{e}}}{\varepsilon_{\text{e}} + N_j(\varepsilon_{\text{i}} - \varepsilon_{\text{e}})}}{1 - \frac{f}{3}\sum\limits_{j=x,y,z} \frac{N_j(\varepsilon_{\text{i}} - \varepsilon_{\text{e}})}{\varepsilon_{\text{e}} + N_j(\varepsilon_{\text{i}} - \varepsilon_{\text{e}})}} \qquad (MG) \tag{8}$$

and the effective permittivity according to the Bruggeman reads [3]

$$\varepsilon_{\mathrm{eff}} = \varepsilon_{\mathrm{e}} + \frac{f}{3}(\varepsilon_{\mathrm{i}} - \varepsilon_{\mathrm{e}}) \sum_{j=x,y,z} \frac{\varepsilon_{\mathrm{eff}}}{\varepsilon_{\mathrm{eff}} + N_j(\varepsilon_{\mathrm{i}} - \varepsilon_{\mathrm{eff}})} \qquad (BS) \tag{9}$$

These equations are derived for small volume fractions of inclusions. In general, the same restrictions apply for mixtures of ellipsoids as for mixtures of spheres. With small-volume fractions of ellipsoids, (MG) is more accurate and with high-volume fractions of ellipsoids (BS) is more applicable.

2.2.3 Nonlinear composites

The mixing equations presented in the previous section hold for mixtures of linear composites. Linearity means that the dipole moment induced in the molecules of the material depends linearly on the electric field. However, there are non-linear materials for which this relation does not hold. As a result, the effective permittivity depends on the amplitude of the applied electric field. Ferroelectrics are an example of non-linear materials. They are materials for which permittivity can be changed by applying a biasing electric field. Tunability is defined as the ratio of the maximum to the minimum permittivity:

$$n = \varepsilon_{\mathrm{eff}}(0)/\varepsilon_{\mathrm{eff}}(E_b) \tag{10}$$

where $\varepsilon_{\mathrm{eff}}(0)$ is the permittivity without the biasing field and $\varepsilon_{\mathrm{eff}}(E_b)$ is the permittivity with the biasing electric field. The permittivity with the biasing field is smaller than without the biasing field. Both of these are functions of the volume fraction of ferroelectric inclusions. In addition to large tunability, it is usually desirable to have low losses. A figure of merit for a tunable material which measures both quantities at the same time is defined as [51]

$$K = \frac{(n-1)^2}{n \tan\delta_0 \tan\delta_E} \tag{11}$$

where $\tan\delta_E$ is the loss tangent of the composite with the biasing field and $\tan\delta_0$ is the loss tangent without the biasing field. This is so-called Quality Factor of a Tunable Component (QFTC).

Traditionally, the effective permittivity of a mixture of a linear and nonlinear dielectric has been derived by writing a similar expansion for the effective permittivity of a tunable composite with applied biasing field as can be written for tunable homogenous materials:

$$\varepsilon_{\mathrm{eff}} = \varepsilon_{\mathrm{eff}}(0) + aE^2 \tag{12}$$

where $\varepsilon_{\text{eff}}(0)$ is the effective permittivity without the biasing field, E is the biasing electric field strength and a is a coefficient that needs to be solved [52, 53]. In [20], this approach has been combined with the balance in the stored electrical energy and the rate of the energy dissipation. An interesting result has been found in that the tunability of a ferroelectric increases when adding a small amount of non-tunable dielectric to form a tunable composite. The explanation was that due to the distribution of the electric field, the electric field is concentrated into the tunable material phase. According to experimental studies for the example in [16, 17, 19] the tunability of a pure ferroelectric has found to decrease, not increase when adding a small amount of non-tunable dielectric to the ferroelectric. In those studies, it was also pointed out that although the tunability decreases, these composite materials are still interesting because of reduced losses.

Also the analysis based on the (MG) mixing equation shows that the local field inside the ferroelectric decreases, not increases when adding non-tunable spheres to the ferroelectric background. As a result, the tunability also decreases. The biasing electric field changes the permittivity of the ferroelectric, but is always much higher than the permittivity of the linear dielectrics. The electric field is focused inside the dielectric spheres with smaller permittivity than the surrounding ferroelectric. The electric field in the ferroelectric cannot be enhanced at the same time when the global average field remains constant. Let us write an approximation for a composite which consists of a ferroelectric background and a small amount of dielectric spheres. The local field in the ferroelectric phase can be written with the (MG) approximation using Eq. (1), (2) and (4) as

$$E_L = E_{\text{ave}}(1 + f/2)^{-1} \tag{13}$$

where f is the volume fraction of dielectric spheres. It is assumed that the permittivity of the ferroelectric is much larger than the permittivity of the dielectric. It can be seen that adding a small amount of dielectric spheres decreases the local electric field in the ferroelectric.

A disadvantage of traditional models is that the tunability as a function of the volume fraction of inclusions has a singularity, where the tunability approaches infinity. There is no physical explanation for this singularity and it has not been found experimentally. It seems that the singularity is just an artifact due to the analytical approach used. In this thesis, a new approach is used to derive a model for the effective permittivity and tunability of a mixture of ferroelectric and ordinary dielectric. The model is continuous without any singularities and the tunability decreases when adding dielectric material to the ferroelectric material.

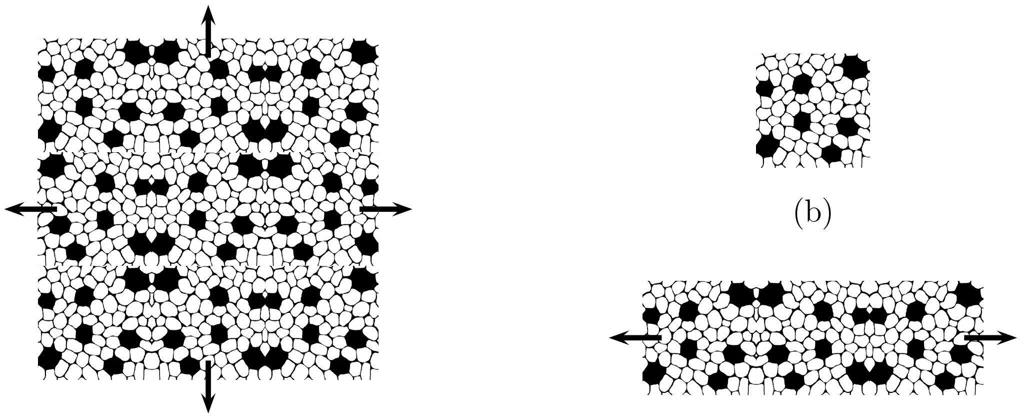
2.3 Numerical methods

In this section, an overview to different simulation methods is given to solve the effective permittivity. The focus is in three dimensional composites, where the wavelength is much longer than the scale of inhomogeneities. Detailed description of numerical methods is not included.

The effective permittivity as a function of volume fraction of inclusions can be solved by computing the effective permittivity for each volume fraction of inclusions numerically. This seemingly straightforward approach has many problems, some of which are often neglected. The focus in this thesis is on composites with random microstructure. There are several studies about the numerical modeling of periodic composites, for example [54, 55]. The vast majority of these models are not designed for any specific material and the authors do not advise readers to use models for random composites. They are most often derived and used for ordered composites, for which they are well suited. Sometimes periodical models are used to model random composites, for example in [56]. Therefore the use of the periodical models for random composites is discussed briefly.

2.3.1 Boundary conditions

The computation domain needs to be terminated with boundary conditions. These boundaries can be periodical, open or a combination of them both. Illustrations of different boundary conditions are presented in Fig. 7 as a cross section of a three-dimensional simulation sample. With periodic boundary conditions, the geometry corresponds to an infinite and periodical lattice structure, which is illustrated in Fig. 7 (a). The geometry is repeated infinitely to the directions of arrows. The calculation domain is repeated infinitely with its mirror image. In mathematics, these boundary conditions are referred as Dirichlet and Neuman boundary conditions. In engineering world, these boundaries are often called "perfect magnetic conductors" (PMC) and "perfect electric conductors" (PEC). A periodical boundary condition can also be constructed so that the neighboring cube is a copy of the original instead of the mirror image. This can be achieved by requiring that the field or the potential in the boundary is identical to the field on the opposite side of the boundary. The periodical boundary condition is a natural choice with "finite element methods" (FEM) or with "finite difference methods" (FD), because there also the space between inclusions is discretized. With FEM, periodical boundary conditions represent the simplest possible boundary conditions. With integral equation based methods, such as with the boundary integral equation (BEM) method, the periodical boundary condition is more complex to introduce. In [57], the periodical boundary condition is introduced to BEM by discretizing inclusions and the surfaces of the outer boundaries of the calculation domain.



(a) (b) (c)

Figure 7: Illustration of the simulation space with three different boundary conditions: (a) periodical (simulated sample repeated infinitely in all directions), (b) open (sample in free space) and (c) combination of these (simulation repeated infinitely inside a slab, which is surrounded with the free space).

With open boundary conditions (Fig. 7 (b)), the simulated sample is surrounded by free space. This type of boundary condition is a natural choice with boundary integral equation-based methods or when using the T-matrix method [58]. There only the surface of each inclusion is discretized and all inclusions are placed in a homogenous infinite background. In fact there are boundary conditions only on the surface of each inclusion in the simulation. In practice, the simulation is sometimes described to have open- or radiation boundary conditions just to distinguish it from the simulation space shown in Fig. 7 (a). With FEM and FD the introduction of the open boundary requires the introduction of an absorbing layer, because also the background of inclusions needs to be discretized. As a result, with FEM or FD the open boundary condition is not as popular as the periodical one, when simulating the effective permittivity of a composite.

In Fig. 7 an example of combination of open and periodical boundary conditions is presented. The example corresponds to a slab of material with periodicity in two directions that form an infinite layer. The slab is surrounded by free space. This geometry requires the introduction of periodic boundary conditions into the integral equation method or the introduction of absorbing boundary conditions to FEM or FD.

2.3.2 Solving the effective permittivity

The effective permittivity can be solved once the potential or the electric field is known. When modeling low-loss composites with very small inclusion size are compared to the wavelength, it is often enough to solve only the static electric field. When periodical boundary conditions illustrated in Fig. 7 (a) with a cubical computation domain are chosen, the effective permittivity can be calculated by averaging the electric flux across the unit cell:

$$\varepsilon_{\text{eff}} = \frac{1}{aU} \int \mathbf{D} \cdot d\mathbf{A} \tag{14}$$

where a is the length of the side of the cube, U is the static electric voltage applied across the sample, D is the electric flux and A is the surface of the cube.

With open boundary conditions (Fig. 7 (b)), solving the effective permittivity is more complicated. The effective permittivity needs to be solved from the scattered field of the sample by comparing it to a particle with the same shape as the material sample but with homogenous permittivity. The effective permittivity is the same as the permittivity of a homogenous sample which produces the same scattered field as the sample of composite material. In [59], this approach is used by making the material sample to be spherical. Because the shape of the material sample needs to be modeled accurately with a collection of inclusions of the composite material, the number of inclusions needs to be very large.

Boundary conditions that correspond to a material slab (Fig. 7 (c)) are a natural choice if electrostatic simulations cannot be used. Then the effective permittivity can be solved from the transmitted and reflected power, when the slab is illuminated from one side. It has been shown [60], that the homogenization procedure related to this design can sometimes be problematic, especially with resonant inclusions. Another problem is that the calculated effective permittivity of a thin material layer might not correspond to the effective permittivity of a bulk material. The physical reason is that the polarization of inclusions near the surface of the layer is different from that of the inclusions deep inside the material. For example in [61], the effective permittivity of a disordered ceramic/polymer composite is modeled as a slab of an array of small spheres. There the effective permittivity is found to increase when the size of spheres decreases. The size of spheres is compared to the overall thickness of the slab. Therefore decreasing the size of spheres corresponds to increasing the number of spheres in the slab. The number of inclusion layers changes the calculated permittivity, when the number of spheres is small. If, instead of a slab of an array of spheres, an infinite array of spheres were used, the effective permittivity would not be dependent on the size of the spheres.

2.3.3 Model for the geometry of the composite

It is enough to solve the electric field inside a single unit cell, when periodical boundary conditions are used. However, if the modeled structure is random, modeling the composite with regular lattice might not be the best choice. Even in the case where the simulated effective permittivity seems to agree well with the experimentally measured values, one needs to ask if the model has any capability to predict the effective permittivity for some other material combination. For example, in [56] the effective permittivity of a ceramic/polymer composite with random arrangement of ceramic inclusions is simulated with a regular lattice of hollow cylinders. If one wishes to use this study to predict the effective permittivity of some other material combination, the modeling method is problematic. In that case, it is not clear how parameters of the cylinder should be chosen.

Periodical composites are, in general, much simpler to model than composites with randomness. The real life composites with randomness have typically highly complex microstructures. Both the shape of inclusion and the arrangement can have randomness. In addition, inclusions might have a significant size distribution. In practice, everything cannot be included in the model. There are various approaches to modelling the randomness. One approach is to take, for example, a regular cubic or honeycomb lattice and to randomly fill the unit cells with two different materials [57, 62, 63]. Another approach is to simulate the randomness by choosing a basic shape for inclusions and placing them into random positions within the simulation domain [34].

The effective permittivity depends on the arrangement of inclusions, if the simulation space is not very large compared to the size of inclusions. Therefore a common approach is to choose as large of a simulation domain as possible. If the domain is large enough, the calculated effective permittivity should not change significantly if another random arrangement of inclusions is used. There is a practical problem in this approach: when the number of particles increases, the number of unknowns increases as well. As a result, the number of unknowns that are used to describe the shape of individual inclusions in the mixture is usually reduced when the computation domain is increased. In [64], the number of unknowns is reduced to the limit where only a few unknowns describe each scatterer. In that case it is impossible to realistically model the complex field distribution inside or near the inclusions. As a result, the electric field distribution inside the sample might differ greatly from the electric field distribution inside the real sample that has been modeled. The effective permittivity is an averaged quantity and therefore it is sometimes assumed, that there is no need to model the microstructure of the material realistically. However, the microgeometry highly affects the macroscopic properties of the composite. It is shown, for example, analytically [65] and numerically in [66], and experimentally in many studies [67–69]. In light of these studies, numerical methods that do not pay any attention to the microstructure of the material seem not to be reliable.

Instead of increasing the size of the computation domain, one can use the so-called Monte Carlo simulations. In the Monte Carlo method, several random samples are created. The effective permittivity is solved for each sample. The effective permittivity is approximated to be the average over all individual Monte Carlo samples. When using the Monte Carlo method, the estimate for the effective permittivity is solved using several realizations. The problem has been that Monte Carlo samples have had to be still relatively large [34], otherwise the deviation of the results is too large. In that case the necessary amount of simulation samples is large. It has not been clear if the size of the sample has a significant effect on the effective permittivity. A solution for both of these problems is suggested in this thesis.

3 Summary of publications

The goal of the thesis was to develop modeling methods for the modeling of composites for material design applications. The hypothesis was that the microstructure of the material plays a significant role, although sometimes it has been neglected. The focus in [P1-P3] is in numerical modeling of composites and the focus in [P4-P5] is in analytical modeling. In [P1] a novel method to reduce the computational cost of numerical modeling is introduced. The method is then applied to model the effective permittivity of a ceramic/polymer composite [P2]. The modeled effective permittivity is in good agreement with the experimental results. In [P3] some problems related to the modeling of composites are discussed. A new analytical method especially for disordered composites with high electrical contrast is derived in [P4]. The equation combines the desirable properties of two of the most popular mixing equations. Therefore it is applicable with all volume fraction combinations of materials. In [P5] a new method to calculate the effective permittivity of a mixture of linear and non-linear dielectrics is introduced and it is compared to numerical and experimental values found in the literature. Tunable composites have not been widely analytically studied. It seems that this is the first non-singular solution for the effective permittivity and tunability of a ferroelectric/polymer composite. The equation can easily be applied for other material combinations as well.

3.1 Micro structure based numerical modeling

In publications [P1-P3] numerical modeling of composites is discussed. In [P1] the numerical effort of modeling of composites is reduced by a novel averaging method. As a result, the microstructure can be better taken into account, which is shown in [P2]. In [P3] problems related to the modeling of the effective permittivity with the so-called connectivity approach are pointed out.

3.1.1 Reducing computational cost [P1]

A three-dimensional random mixture of spheres is studied. Spheres occupy random positions in a cubic sample and they are allowed to overlap and form clusters. The static effective permittivity is solved for several Monte-Carlo samples using the FEM method with periodic boundary conditions. For each random sample, the effective permittivity is solved three times with orthogonal voltage orientations. Accordingly, for each sample there are three estimates for the effective permittivity: ε_x, ε_y and ε_z. The effective permittivity of each Monte Carlo sample is calculated as an average of them. Permittivities ε_x, ε_y and ε_z are not independent random variables. For instance, if spheres are located so that they form a chain-like cluster that connect walls of the cube, the permittivity of ε_x is larger than ε_y or ε_z. When the effective permittivity is calculated as an average over these three samples, the estimate for the effective permittivity of this realization is better than using only one field direction.

There were two different sets of simulations. In one set, the radius of spheres was ten times smaller than the side of the cube (large domain) and in the other set it was only five times smaller (small domain). Simulations were performed in a super computer in the Finnish IT Center for Science to be able to have a high numerical accuracy in both sets of simulations. In simulations with a large domain, the volume of the calculation domain was eight times larger than that in simulations with a small domain. As a result, the number of unknowns in the larger set of simulations was about eight times the number of unknowns in the smaller set.

A very interesting result was that after averaging, the deviation of the estimated effective permittivity was about the same for both sets of simulations. Also the effective permittivity as a function of volume fraction of inclusions was about the same for both sets of simulations. As a result, the smaller set of simulations can be used as well as the larger set of simulations, when the special averaging method is used. Without the averaging, the deviation was too large with a small computation domain. This result shows that it is possible to use much smaller computation domain than had been traditionally used. As a result, each scatterer can be modeled with more unknowns because there is no need to waste unknowns in order increase the computation domain.

3.1.2 Application to ceramic/polymer composite [P2]

A method developed in [P1] was applied to model the effective permittivity of a ceramic/polymer composite that consisted of titanium dioxide powder mixed with epoxy in (see Fig. 1). The study was made in co-operation with Microelectronics and Materials Physics Laboratories and EMPART Research Group of Infotech Oulu, where the samples were manufactured and the effective permittivity was measured. The wavelength of the applied electric field was much larger than the size of inclusions and therefore static field simulations were used.

In simulations, inclusions were placed into random positions in a cubical sample and the averaging method developed in [P1] was used. A scanning electroscope picture of the ceramic powder is shown in Fig. 2. The picture of the powder shows both powder clusters and individual particles. Unfortunately the scanning electron microscope picture of the composite in Fig. 1 does not reveal the exact microstructure, because the epoxy blurs the picture. A very simplified model for inclusions was used. They were assumed to approximately follow the lattice structure of the rutile phase of the titanium dioxide. This simplification was made, because there were no better estimates available.

The effective permittivity of the composite as a function of volume fraction of ceramic is shown in Fig. 8 and Fig. 9. In Fig. 8 simulation results are shown before averaging of three field directions of each sample and in Fig. 9 after averaging. The simulated effective permittivity is in good agreement with the measurements with all volume fractions of inclusions in Fig. 9. The result suggests that the averaging method developed in [P1] can be applied to model the effective permittivity of real life composites.

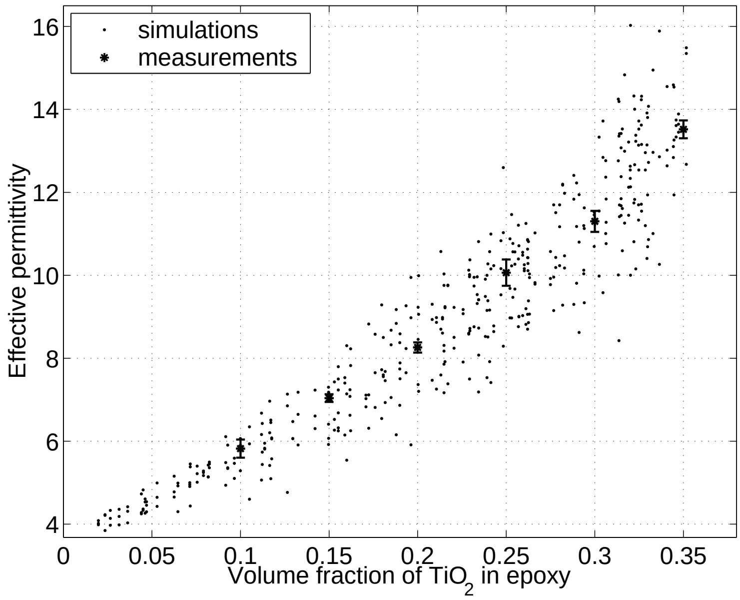


Figure 8: Simulated effective permittivity of a titanium dioxide/epoxy composite as a function of the volume fraction of titanium dioxide. Simulations are shown before averaging the three estimates of the effective permittivity of each Monte Carlo sample. Therefore for each simulated volume fraction of inclusions, there are three effective permittivity values.

3.1.3 Connectivity approach and checker board geometries [P3]

Composites are often characterized by their connectivity. In a two-phase composite there are ten different connectivity possibilities. Phases can be connected either in 0, 1, 2, or 3-dimensions. For example, when a small amount of ceramic is mixed with epoxy, it can be characterized as 0-3 connectivity. The epoxy has connectivity in all three dimensions and the ceramic in 0 dimensions,

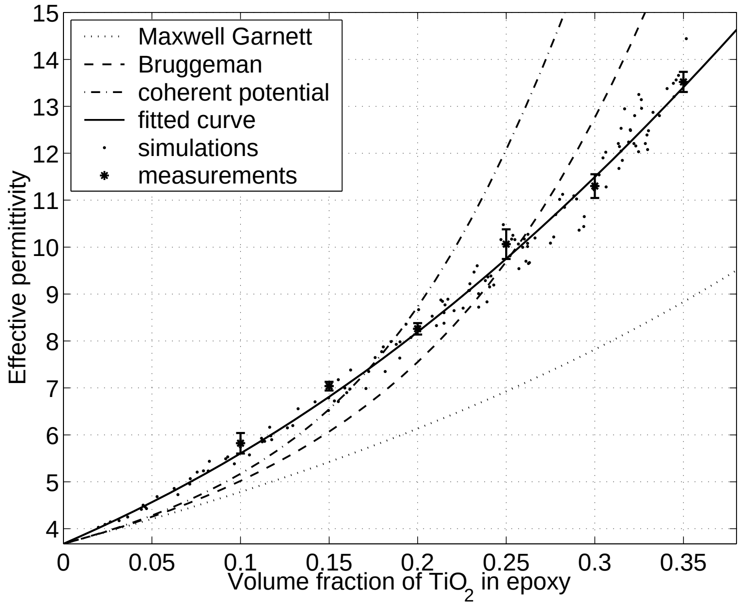


Figure 9: As Fig. 8, but now the effective permittivity of each Monte Carlo sample is averaged over the values calculated with three orthogonal field directions. The deviation is therefore highly reduced. Predictions of some mixing models are also presented.

because individual ceramic inclusions are separated. On the left side of Fig. 10, an illustration of a two-dimensional correspondence of the 0-3 connectivity is presented. The black phase is connected in 0 directions and the white phase is connected in all 3 directions. On the right side of Fig. 10, an example of a two-dimensional 1-1 connectivity is shown. There both white and black phases are connected in one direction, but disconnected to the other.

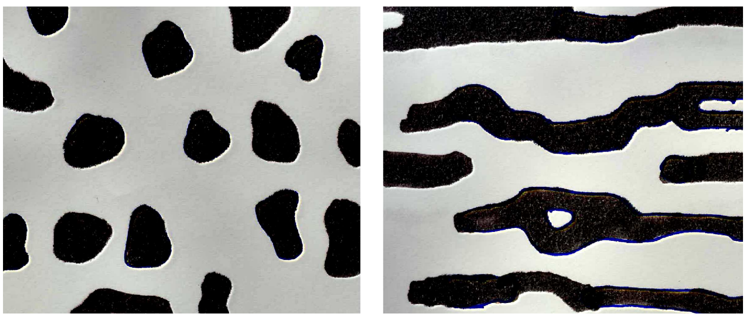


Figure 10: Illustrations of 0-3 and 1-1 connectivities.

This classification of composites might lead to a temptation to use simple circuit models that take the connectivity into account [70–73]. There it is assumed, that the composite is sliced into small cubes. Each cube is connected to surrounding cubes to form a network. Inside each cube, there is only one material phase. The network of cubes can be modeled as a network of capacitors. All capacitors are connected and the capacitance of the whole system can be solved. This also gives the effective permittivity of the whole composite. This method is called the mixed connectivity method.

In [P3] it is shown using numerical simulations for a three dimensional checkerboard mixture that the effective permittivity calculated using mixed connectivity models fails. The effective permittivity of the checkerboard mixture was solved with different electrical contrast between the two material phases. The accuracy with the largest electrical contrast of 100 is not sufficient and the simulated effective permittivity is supposedly overestimated.

The reason for the failure of the mixing connectivity model is clear. In Fig. 3 of [P3], the electric potential lines inside of the simulated structure are shown. In the circuit model approach, the electric field inside each capacitor should be constant. In the circuit model, the boundaries of individual capacitors are replaced with ideal electric and magnetic conductors. This can only be done, if such a replacement does not change the electric field distribution inside the material. In this case, the material boundaries cannot be replaced with ideal electric and magnetic conductors. As a result, the effective permittivity calculated from the circuit model is different from the simulated effective permittivity values. If the electrical contrast is small, say five or less, all analytical methods for the effective permittivity of the mixture predict very close to the same permittivity. In this range, the effective permittivity as a function of volume fraction of inclusions for classical mixing theories is approximately linear. For the checker board composite, the effective permittivity is therefore very close to the arithmetic average of mixed materials. When the electrical contrast increases, the mixed connectivity approach fails drastically.

3.2 Microstructure based analytical modeling

In this section, the author's own contribution to the analytical modeling of composites is introduced. The aim of the study was to develop analytical methods for composite designing applications. Models do not involve any adjustable parameters. Special features of artificial composites are taken into account when developing the models. These often include low losses, small grain size compared to the wavelength and sometimes a high electrical contrast between the permittivities of materials. An important feature of models is that they are applicable with all volume fractions of inclusions.

3.2.1 Analytical model for composite design applications [P4]

The motivation behind the publication [P4] was the following: suppose one needs to find an ideal material combination for a two phase ceramic/polymer composite. The volume filling ratio of inclusions is not restricted and the electrical contrast between the two material phases can be high. The question could be, for example, how the shape of inclusions affects the effective permittivity of the composite. The permittivity of a polymer is low, if small losses are required, but the permittivity of the ceramic can be as high as several thousands. Obviously, the loading of the ceramic should be as high as possible to maximize the permittivity. There are two good mixing equations to choose from: Maxwell Garnett (MG) and Bruggeman symmetric (BS). The BS mixing equation should be better with high volume filling loadings of inclusions, but the (MG) is more accurate with small volume filling loadings. If the electrical contrast between inclusions is high, the difference between these two models is large. If one wishes to study the effect of the volume fraction and the shape of inclusions, one should somehow switch between these models.

In [P4] a novel mixing equation is derived. It has MG equation as a low volume filling ratio limit and BS equation as a high volume filling ratio limit. The equation is derived especially for composites with high contrast between the inclusion and the background phase. Therefore it is applicable even for modeling the effective conductivity of composites consisting of conducting inclusions in a non-conductive background. The model is valid for spherical and ellipsoidal inclusions and it does not involve any adjustable parameters.

Usually the MG mixing equation fails with large volume filling ratios of inclusions, because the small volume filling ratio is assumed. In the derivation of the MG equation (Eq. 4), the interaction between distant inclusions is calculated by assuming that the environment has the permittivity of ε_{e}. However, the assumption is not valid when calculating far field interactions of inclusions with high volume filling fractions of inclusions. The surrounding space should have the permittivity $\varepsilon_{\mathrm{eff}}$ rather than ε_{e}. In the BS theory this problem is avoided, because each inclusion is always embedded into a background with permittivity $\varepsilon_{\mathrm{eff}}$, but there is some error with small volume fractions of spheres.

In [P4] a differential equation for the effective permittivity is derived. It starts with an MG type of equation with small volume fractions of spheres, but it moves towards the BS equation when the volume fraction of spheres increases. The resulting equation for the effective permittivity can easily be solved numerically, or a solution for the inverse function can be used. The solution is compared to numerical and experimental results found in the literature. It seems that the new equation is a good alternative in a case when all volume fractions of inclusions need to be modeled analytically and the choice between BS and MG cannot be made.

3.2.2 Electrically tunable composite [P5]

Because of the singularities of existing mixing equations for tunable composites, a novel method to calculate the effective permittivity and the tunability of such a composite is presented in [P5]. The composite is assumed to consist of spherical inclusions and all volume fractions of composites are studied. Only those volume fractions of a material are interesting, where the material is tunable. Therefore the volume fraction of a ferroelectric cannot be very small. As a result, the Bruggeman effective medium theory is sufficient to be utilized with all volume fractions of inclusions.

For the permittivity of the ferroelectric, a model presented in [74] is used. The permittivity of the ferroelectric depends on the electric field that is applied across the ferroelectric material. If the ferroelectric material is dispersed as small inclusions inside the composite, one needs to know the local electric field acting on each inclusion. As a result, the electric biasing field needs to be replaced with the local field in the mixture.

The local field is approximated with the Bruggeman effective medium theory. There the surrounding space around a sphere is replaced with material with the effective permittivity. The field inside the sphere can then be solved when the global average field applied over the whole composite is known. In the Bruggeman effective medium theory, the mixture is symmetric. That is to say, either the background phase or the inclusion phase can be modeled as spheres. Therefore the average field inside either of the material phases is calculated by assuming a spherical inclusion and replacing the surrounding material with a material with the permittivity of ε_{eff}.

The effective permittivity is solved from Bruggeman effective medium theory. As a result, there are three unknowns (effective permittivity of the mixture, the internal electric field acting on the ferroelectric material and the permittivity of the ferroelectric) and three equations from which the effective permittivity or tunability as a function of the volume fraction of ferroelectric can be solved.

As an example, two material combinations were studied. The ferroelectric material was mixed with PTFE polymer or with titanium dioxide ceramic. The result was that the tunability decreases when adding non-tunable material to the ferroelectric. This is a reasonable result, although the opposite effect was found in [20]. However, experimental results points to a decreasing tunability [16–19]. The permittivity of the titanium dioxide was much higher than that of the polymer. As a result, the tunability can be achieved with smaller volume fraction loadings of ferroelectric material than with polymer composites would be possible. This might be advantageous in some applications, especially for reducing losses of the tunable material. Losses of ferroelectrics are typically much higher than those of ordinary linear dielectrics. If a sufficient tunability can be achieved with a smaller volume filling loading of the ferroelectric material, losses can be reduced. A significant reduction in losses was found experimentally in [16]. According to analytical results in [P5] one should prefer dielectrics with as high permittivity as possible in tunable composites, because then the losses can be most effectively reduced because lower volume filling ratios of ferroelectric material can be used. The tunability should also be increased with needle- or disk-like ferroelectric inclusions, in order that the percolation would occur with smaller volume fractions of inclusions than when using spherical inclusions.

3.3 Main contributions

The main findings of the thesis can be summarized as follows:

- Development of a new method to calculate effective material parameters. The method can be used with any numerical simulations and it can save both computation memory and time.
- Application of the modeling method to a practical composite.
- Numerical modeling of a checkerboard geometry to demonstrate drawbacks related to simple circuit model based connectivity calculations.
- Derivation of a new analytical mixing equation for ellipsoidal and spherical inclusions that combines desirable properties of Maxwell Garnett and Bruggeman equations.
- Derivation of a new analytical model for the effective permittivity and tunability of a ferrolectric/dielectric composite.

References

[1] J. D. Jackson. *Classical Electrodynamics*. John Wiley and Sons, University of California, Berkeley, 1999.

[2] R. P. Feynman, R. B. Leighton, and M. Sands. *Lectures on Physics*, volume 2. Addison-Wesley publishing Company, California Institute of Technology, 1964.

[3] A. Sihvola. *Electromagnetic mixing formulas and applications*. IEE Electromagnetic Waves Series 47, The Institution of Electrical Engineers, 1999.

[4] L. Solymar and D. Walsh. *Lectures on the Electrical Properties of Materials*. Oxford University Press, Oxford, 1991.

[5] P. Robert. *Electrical and Magnetic Properties of Materials*. Artech House, Norwood, MA, 1988.

[6] P. S. Neelakanta. *Electromagnetic Materials, monolithic and composite versions and their applications*. CRC Press, Boca Raton, 1995.

[7] B. K. P. Scaife. *Principles of Dielectrics*. Oxford Science Publications, Walton Street, Oxford, 1989.

[8] A. R. Hippel. *Dielectric Materials and Applications*. Artech House, Boston, London, 1995.

[9] A. Moulson and J. Herbert. *Electroceramics*. John Wiley and Sons, 2003.

[10] H. Jantunen. *A novel Low Temperature Co-firing Ceramic (LTCC) material for telecommunication devices*. PhD thesis, Department of Electrical Engineering and Infotech Oulu, University of Oulu, 2001.

[11] P. Chahal, R. R. Tummala, M. G. Allen, and M. Swaminathan. A novel integrated decoupling capacitor for MCM-L technology. *IEEE Transactions on Components, Packaging, and Manufacturing Technology- Part B*, 21(2):184–193, 1998.

[12] C.J. Dias, R. Igreja, R. Marat-Mendes, P. Inácio, J.N. Marat-Mendes, and D. K. Das-Gupta. Recent advances in ceramic-polymer composite electrets. *IEEE Transactions on Dielectrics and Electrical Insulation*, 11(1):35–40, 2004.

[13] A. Sugita, K. Suzuki, and S. Tasaka. Ferroelectric properties of a triphenylene derivate with polar functional groups in the crystalline state. *Physical Review B*, 69:212201, 2004.

[14] H. Xu, J. Zhong, X. Liu, J. Chen, and D. Shen. Ferroelecric and swithcing behavior of poly(vinylidene fluoride-trifluoroethylene) copolymer ultrathin films with polypyrrole interface. *Applied Physics Letters*, 90:092903, 2007.

[15] N. A. Hakeem, H. I. Abdelkader, N. A: El-sheshtawi, and I. S. Eleshmawi. Spetroscopic, thermal and elecrical investigations of PVDF films filled with $BiCl_3$. *Journal of Applied Polymer Science*, 102:2125–2131, 2006.

[16] L. C. Sengupta and S. Sengupta. Breakthrough advances in low loss, tunable dielectric materials. *Material Research Innovations*, 2:278–282, 1999.

[17] B. Su and T. W. Button. Microstructure and dielectric properties of Mg-doped barium strontium titanate ceramics. *Journal of Applied Physics*, 95(3):1382–1385, 2004.

[18] K. F. Astafiev, V. O. Sherman, A. K. Tagantsev, and N. Setter. Can the addition of a dielectric improve the figure of merit of a tunable material? *Journal of the European Ceramic Society*, 23(14):2381–2386, 2003.

[19] Y. Chen, X. Dong, R. Liang, J. Li, and Y. Wang. Dielectric properties of $Ba_{0.6}Sr_{0.4}TiO_3/Mg_2SiO_4/MgO$ composite ceramics. *Journal of Applied Physics*, 98:064107, 2005.

[20] V. O. Sherman, A. K. Tagantsev, N. Setter, D. Iddles, and T. Price. Ferroelectric-dielectric tunable composites. *Journal of Applied Physics*, 99:074104, 2006.

[21] D. S. McLachlan. An equation for the conductivity of binary mixtures with anisotropic grain structures. *Journal of Physics C*, 20(7):865–877, 1987.

[22] D. S. McLachlan, M. Blaszkiewicz, and R. E. Newnham. Electrical resistivity of composites. *Journal of American Ceramic Society*, 73:2187, 1990.

[23] R. Diaz, W. Merrill, and N. Alexopoulos. Analytic framework for the modeling of effective media. *Journal of Applied Physics*, 84(12):6815–6826, 1998.

[24] C. Brosseau, P. Quéffélec, and P. Talbot. Microwave characterization of filled polymers. *Journal of Applied Physics*, 89(8):4532–4540, 2001.

[25] C. Brosseau. Generalized effective medium theory and dielectric relaxation in particle-filled polymeric resins. *Journal of Applied Physics*, 91(5):3197–3204, 2002.

[26] T. K. H. Starke, C. Johnston, S. Hill, P. Dobson, and P.S. Grant. The effect of inhomogeneities in particle distribution on the dielectric properties of composite films. *Journal of Physics D: Applied Physics*, 39:1305–1311, 2006.

[27] J. C. Maxwell Garnett. Colours in metal glasses and metal films. *Transactions of the Royal Society*, CCIII:385–420, 1904.

[28] D. A. G. Bruggeman. Berechnung verschiedener physikalischer Konstanten von heterogenen Substanzen, I. Dielektrizitätskonstanten und Leitfähigkeiten der Mischkörper aus isotropen Substanzen. *Annalen der Physik*, 24(5):636–664, 1935.

[29] O. F. Mossotti. Discussione analitica sull'influenza che l'azione di un mezzo dielettrico ha sulla distribuzione dell'elettricità alla superficie di più corpi elettrici disseminati in esso. *Memorie di Matematica e di Fisica della Societa Italiana delle Scienze*, XXIV(Parte seconda):49–74, 1850.

[30] R. J. E. Clausius. *Die mechanische Behandlung der Electricität*. Abschnitt III, F. Vieweg, Braunschweig, 1879.

[31] Lord Rayleigh. On the influence of obstacles arranged in rectangular order upon properties of the medium. *Philosophical Magazine*, 34:481–502, 1892.

[32] G. Kristensson. Homogenization of spherical inclusions. *Progress In Electromagnetic Research*, 42:1–25, 2003.

[33] J. Lam. Magnetic permeability of a simple cubic lattice of conducting magnetic spheres. *Journal of Applied Physics*, 60(12):4230–4235, 1986.

[34] K. K. Kärkkäinen, A. H. Sihvola, and K. I. Nikoskinen. Analysis of a three-dimensional dielectric mixture with finite difference method. *IEEE Transactions on Geoscience and Remote Sensing*, 39(5):1013–1018, 2001.

[35] D. A. Robinson and S. P. Friedman. The effective permittivity of dense packings of glass beads, quarz sand and their mixtures immersed in different dielectric backgrounds. *Journal of Non-Crystalline Solids*, 305:261–267, 2002.

[36] J. P. Calame. Finite difference simulations of permittivity and electric field statistics in ceramic-polymer composites for capacitor applications. *Journal of Applied Physics*, 99:084101, 2006.

[37] D. Polder and J. H. van Santeen. The effective permeability of mixtures of solids. *Physica*, 12(5):257–271, 1946.

[38] G. P. de Loor. Dielectric properties of heterogeneous mixtures containing water. *The Journal of Microwave Power*, 3:67–73, 1968.

[39] C. J. F. Böttcher. *Theory of electric polarization.* Amsterdam:Elsevier, 1952.

[40] G. Grimvall. *Thermophysical properties of materials.* North-Holland, Amsterdam, 1986.

[41] M. T. Clarkson. Electrical conductivity and permittivity measurements near the percolation transition in a microemulsion. 2. interpretation. *Physical Review A*, 37(6):2079–2090, 1988.

[42] W. E. Kohler and G.C. Papanicolaou. *Multiple Scattering and Waves in Random Media.* P. L. Chow and W. E. Kohler and G.C. Papanicolaou Eds., New York: North Holland, 1981.

[43] R. J. Elliott, J. A. Krumhansl, and P. L. Leath. The theory and properties of randomly disordered crystals and related physical systems. *Reviews of modern physics*, 46(3):465–543, 1974.

[44] P. N. Sen, C. Scala, and M. H. Cohen. A self-similar model for sedimentary rocks with application to the dielectric constant of fused glass beads. *Geophysics*, 46(5):781–795, 1981.

[45] H. Looyenga. Dielectric constants of heterogenous mixtures. *Physica*, 31:401–406, 1965.

[46] K. Lichtenecker. Die dielektrizitätkonstante natürlicher und Künstlicher Mischkörper. *Physikalische Zeitschrift*, 27(4):115–158, 1926.

[47] W. M. Merrill, R. E. Diaz, M. M. LoRe, M. C. Squires, and N. G. Alexopoulos. Effective medium theories for artificial materials composed of multiple sizes of spherical inclusions in a host continuum. *IEEE Transactions on Antennas and Propagation*, 47(1):142–148, 1999.

[48] H. Fricke. The Maxwell-Wagner dispersion in a suspension of ellipsoids. *Journal of Physical Chemistry*, 57:934–937, 1953.

[49] W. S. Weiglhofer. Electromagnetic depolarization dyadics and elliptic integrals. *Journal of Physics A*, 31(34):7191–7196, 1998.

[50] J. A. Osborn. Demagnetizing factors of the general ellipsoid. *Physical Review*, 67(11-12):351–357, 1945.

[51] I. B. Vendik, O. G. Vendik, and E. L. Kollberg. Commutation quality factor of two-state switchable devices. *IEEE Transactions on Microwave Theory and Techniques*, 48:802–808, 2000.

[52] D. Stround and P. M. Hui. Nonlinear susceptibilities of granular matter. *Physical Review B*, 37(15):8719–8724, 1988.

[53] D. Stround and V. E. Wood. Decoupling approximation for the nonlinear-optical response of composite media. *Journal of the Optical Society of America B*, 6(4):778–786, 1989.

[54] E. Tuncer, S. M. Gubanski, and B. Nettelblad. Dielectric relaxation in dielectric mixtures: Application of the finite element method and its comparison with dielectric mixture formulas. *Journal of Applied Physics*, 89(12):8092–8100, 2001.

[55] B. Sareni, L. Krähenbühl, A. Beroual, , and C. Brosseau. Effective dielectric constant of periodic composite materials. *Journal of Applied Physics*, 80(3):1688–1696, 1996.

[56] S. Orlowska, A. Beroual, and J. Fleszynski. Barium titanate particle model inquiry through effective permittivity measurements and boundary integral equation method based simulations of the $BaTiO_3$-epoxy resin composite material. *Journal of Physics D: Applied Physics*, 35:2656–2660, 2002.

[57] B. Sareni, L. Krähenbühl, A. Beroual, A.Nicolas, and C. Brosseau. A boundary integral equation method for the calculation of the effective permittivity of periodic composites. *IEEE Transactions on Magnetics*, 33(2):1580–1583, 1997.

[58] W. C. Chew, J. A. Friedrich, and R. Geiger. A multiple scattering solution for the effective permittivity of a sphere mixture. *IEEE Transactions on Geoscience and Remote Sensing*, 28(2):207–214, 1990.

[59] A. von Lerber, J. Sarvas, and J. Pulliainen. Modeling snow volume backscatter combining the radiative transfer theory and the discrete dipole approximation. In *Geoscience and Remote Sensing Symposium, 2006. IGARSS 2006. IEEE International Conference on*, pages 481–484, 2006.

[60] C. R. Simovski and S.A. Tretyakov. Local constitutive parameters of metamaterials from an effective-medium perspective. *Physical Review B*, 75:195111, 2007.

[61] S. Ogitani, S. Bidstrup-Allen, and P. Kohl. Factors influencing the permittivity of polymer/ceramic composites for embedded capacitors. *IEEE Transactions on Advanced Packaging*, 23(2):313–322, 2000.

[62] B. Sareni, L. Krähenbühl, A. Beroual, and C. Brosseau. Effective dielectric constant of random composite materials. *Journal of Applied Physics*, 81(5):2375–2383, 1997.

[63] E. Tuncer, Y. V. Serdyuk, and S. M. Gubanski. Dielectric mixtures: Electrical properties and modeling. *IEEE Transactions on Dielectrics and Electrical Insulation*, 9(5):809–828, 2002.

[64] Y. Wu, X. Zhao, F. Li, and Z. Fan. Evaluation of mixing rules for dielectric constants of composite dielectrics by MC-FEM calculation on 3D cubic lattice. *Journal of Electroceramics*, 11:227–239, 2003.

[65] D. J. Bergman. Nonlinear behavior and 1/f noise near a conductivity threshold: Effects of local microgeometry. *Physical Review B*, 39(7):4589–4609, 1989.

[66] F. Wu and K. Whites. Quasi-static effective permittivity of periodic composites containing complex shaped dielectric particles. *IEEE Transactions on Antennas and Propagation*, 49(8):1174–1182, 2001.

[67] Y. P. Mamunya, Y. V. Muzychenko, P. Pissis, E. V. Lebedev, and M. I. Shut. Processing, structure, and electrical properties of metal-filled polymers. *J. Macromol. Sci.–Phys.*, 40B(3&4):591–602, 2001.

[68] J. K. W. Sandler, J. E. Kirk, I. A. Kinloch, M. S. P. Shaffer, and A. H. Windle. Ultra-low electrical percolation threshold in carbon-nanotube-epoxy composites. *Polymer*, 44(19):5893–5899, 2003.

[69] S. A. Wilson, G. M. Maistros, and R. W. Whatmore. Structure modification of 0-3 piezoelectric ceramic/polymer composites through dielectrophoresis. *Journal of Physics D: Applied Physics*, 38:175–182, 2005.

[70] R. Newnham, D. Skinner, and L. Cross. Connectivity and piezoelectric-pyroelectic composites. *Material Research Bulletin*, 13:525–536, 1978.

[71] H. Banno. Recent developments of piezoelectric ceramic products and composites of synthetic rubber and piezoelectric ceramic particles. *Ferroelectics*, 50:3–12, 1983.

[72] F. Levassort, M. Lethiecq, C. Millar, and L. Pourcelot. Modeling of higly loaded 0–3 piezoelectric composites using a matrix method. *IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control*, 45(6):1497–1504, 1998.

[73] V. Topolov and S. Glushanin. Evolution of connectivity patterns and links between interfaces and piezoelectric properties of two-component composites. *Journal of Physics D: Applied Physics*, 35:2008–2014, 2002.

[74] O. G. Vendik and S. P. Zubko. Modeling the dielectric response of incipient ferrolectrics. *Journal of Applied Physics*, 82(1):4475–4483, 1997.